

## CLAIMS

1. Method for preparing a suspension of a silicic particulate filler, in a silicone material (SM) comprising:

5 > *SM<sub>1</sub>*polyaddition:

- at least one type A polyorganosiloxane POS carrying alkenyl crosslinking functional groups *Fa* capable of reacting with the crosslinking functional groups *Fb* (SiH) of at least one B type POS, this A POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- and at least one B type POS carrying crosslinking functional groups *Fb* (SiH) capable of reacting with the alkenyl crosslinking functional groups *Fa* of the A POS(s);

o and/or *SM<sub>2</sub>*polycondensation:

- at least one C type POS carrying hydroxyl crosslinking functional groups *Fc* and/or OR functional groups (R = C<sub>1</sub>-C<sub>30</sub> alkyl, C<sub>2</sub>-C<sub>30</sub> alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups *Fc'*, these crosslinking functional groups *Fc* being capable of reacting with crosslinking functional groups *Fc* of this C POS or of other C POSs, and with crosslinking functional groups of at least one crosslinking agent *D*, this C POS being taken alone or as a

mixture with at least one nonreactive (E) POS;

➤ and/or  $SM_3$ polydehydrogenocondensation:

- at least one C' type POS carrying hydroxyl crosslinking functional groups  $Fc'$  and/or OR' functional groups ( $R' = C_1-C_{30}$  alkyl,  $C_2-C_{30}$  alkenyl, aryl, which are optionally substituted (preferably halogenated)) precursor of the functional groups  $Fc'$ , these crosslinking functional groups  $Fc'$  being capable of reacting with other crosslinking functional groups  $Fb'$  (SiH) of at least one B' type POS, this C' POS being taken alone or as a mixture with at least one nonreactive (E) POS;
- and at least one B' type POS carrying crosslinking functional groups  $Fb'$  (SiH) capable of reacting with the crosslinking functional groups  $Fb'$  OH or OR' of the C' POS(s);

➤ and/or  $SM_4$ :

- or at least one nonreactive (E) POS;
- this suspension being capable of being used in particular for producing compositions which can be crosslinked by polyaddition and/or by polycondensation and/or by dehydrogenocondensation or antifoam silicone compositions;
- this method being of the type in which an aqueous suspension of silicic particulate filler is made hydrophobic by treating with at least one halogenated

reagent, this treatment comprising a transfer of the silica made hydrophobic into a nonaqueous phase and at least one step for at least partial removal of water,

5 characterized in that:

a) an aqueous silica suspension is prepared or used which comprises:

- ~ silica,
- ~ water which is optionally acidified,
- 10 ~ at least one hydrogen bond stabilizer/initiator,

b) optionally, part of the silicone material SM is incorporated into the aqueous silica suspension obtained at the end of step a);

15 c) hydrophobic units formed by  $\equiv\text{Si}-(\text{R}^c)_1 \text{ to } 3$  with  $\text{R}^c =$  hydrogeno,  $\text{C}_1\text{-C}_{30}$  alkyl,  $\text{C}_2\text{-C}_{30}$  alkenyl, aryl, these groups  $\text{R}^c$  being optionally substituted (preferably halogenated), are grafted onto the silica by  
20 exposing this silica to halosilanes that are precursors of these units and by allowing the reaction to proceed, preferably while stirring the whole, optionally in the hot state;

25 d) the procedure is carried out such that the transfer of the silica grafted by hydrophobic units, from the aqueous phase to the

nonaqueous phase, is carried out;

e) optionally, at least part of the aqueous phase and of the reaction by-products is drawn off;

5 f) the medium is cooled if necessary;

g) optionally, the residual acidity of the nonaqueous phase is washed off;

h) the totality or the remainder of the silicone material *SM* is mixed with the filler  
10 which is now hydrophobic;

i) the residual water is evaporated off;

j) and an oil is recovered which consists of a hydrophobic particulate filler suspension in a crosslinkable silicone material,  
15 preferably without ever passing via a dried hydrophobic silica.

2. Method according to Claim 1, characterized in that the pH of this suspension is  $\leq 2$ , preferably  $\leq 1$ , at least during step a).

20 3. Method according to Claim 1, characterized in that at least one precursor of silicone resin, preferably a silicate, and still more preferably a sodium silicate, is used in step a).

4. Method according to Claim 1,  
25 characterized in that functional units other than hydrophobic units are grafted onto silica by exposing it to halo-silane precursors of these functional grafts,

the functions which can be given to the silica by these units being preferably those in the group comprising the following functions: bactericidal, bacteriostatic, chromophoric, fluorescence, antifouling, and  
5 combinations thereof.

5. Method according to Claim 1, characterized in that there are chosen one or more precipitated silicas whose BET specific surface area is between 50 and 400 m<sup>2</sup>/g and mixing conditions such that  
10 the dynamic viscosity at 25°C of the suspension is less than or equal to 300 Pa.s, preferably less than or equal to 150 Pa.s.

6. Method according to any one of Claims 1 to 5, characterized in that the hydrogen bond  
15 stabilizer/initiator is chosen from organic solvents, preferably from the group comprising alcohols, ketones, amides, alkanes and mixtures thereof.

7. Method according to any one of Claims 1 to 6, characterized in that the acidification of the  
20 aqueous suspension (aqueous phase) is carried out using an acid, preferably an inorganic acid, and still more preferably an acid is chosen from the group comprising: HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> and mixtures thereof.

8. Method according to any one of Claims 1 to 7, characterized in that the silicone material SM  
25 comprises at least one oligoorganosiloxane, preferably a diorganosiloxane, and still more preferably

hexamethyldisiloxane ( $M_2$ ).

9. Method according to any one of Claims 1 to 6, characterized in that the precursor of hydrophobic units is an alkylhalosilane, preferably an alkylchlorosilane, and still more preferably a methylchlorosilane.

10. Method according to any one of Claims 1 to 9, characterized in that a precipitated silica powder is used and in that the following operations are carried out:

- the relevant products are introduced into the stirred preparation vessel in the following order:
  - o the aqueous silica suspension, optionally in several fractions, the hydrogen bond stabilizer/initiator - preferably consisting of isopropyl alcohol, optionally an acid -, preferably HCl -;
  - o a precursor of hydrophobic units:  $-\text{Si}-(\text{R}^c)_{1 \text{ to } 3}$  with  $\text{R}^c = \text{C}_1\text{-C}_{30}$  alkyl or a  $\text{C}_2\text{-C}_{30}$  alkenyl - preferably  $(\text{CH}_3)_3\text{SiCl}-$ ;
  - o part of the SM consisting of at least one oligoorganosiloxane - preferably hexamethyldisiloxane ( $M_2$ )-;
- the medium is heated to a temperature in the region of the reflux temperature of the hydrogen bond stabilizer/initiator - preferably that of isopropyl alcohol between 70 and 80°C;

- the medium is optionally cooled;
- the aqueous phase is separated from the nonaqueous phase - preferably by decantation -;
- the nonaqueous phase is removed;
- 5 • optionally at least once, this nonaqueous phase is washed with an aqueous liquid and then the aqueous washing phase is removed;
- the optionally washed, nonaqueous silicone phase is mixed with all or the remainder of the silicone material *SM*, with the silica now hydrophobic, this
- 10 *SM* preferably comprising at least one polyorgano-siloxane POS;
- an oily suspension of hydrophobic particulate silicic filler is recovered in a crosslinkable
- 15 silicone material *SM*.

11. Method according to any one of Claims 1 to 10, characterized in that the various ingredients are used in the following proportions (parts by dry weight for all that is not water):

- 20 - silica: 100;
- acid (e.g. HCl): 20 to 60, preferably from 30 to 50;
- precursor of  $-\text{Si}-(\text{R}^c)_{1 \text{ to } 3}$  (e.g.  $(\text{CH}_3)_3\text{SiCl}$ ), 5 to 500, preferably from 10 to 200;
- H bond stabilizer/initiator (e.g. isopropanol): 0 to
- 25 20, preferably from 1 to 10;
- *SM* oil: 40 to 2 000, consisting exclusively or otherwise of oligoorganosiloxane - preferably of  $\text{M}_2$ ;

- water: 2 to 8 000, preferably 200 to 1 000.

12.. Method according to any one of Claims 1 to 11, characterized in that the silica used is mainly in the form of a slurry of precipitated silica(s).

13.. Method according to any one of Claims 1 to 12, characterized in that a polyaddition SM is used which contains:

- at least one reactive silicone oil A POS whose crosslinking functional groups Fa are alkenyl - preferably vinyl - functional groups,

this A POS:

- comprising at least two Si-Fa groups per molecule, preferably each situated at one end of the chain,
- and having a dynamic viscosity at 25°C of less than or equal to 250 Pa.s, preferably 100 Pa.s and still more preferably 10 Pa.s,

this A POS being intended to react with the B POS,

- at least one reactive silicone oil B POS, whose crosslinking functional groups Fb are hydrogen functional groups, this B POS comprising at least two groups Si-H per molecule (preferably at least three when the A POS comprises only two Si-Vi groups per molecule), these Si-H groups being advantageously

situated in the chain,

- and/or at least one nonreactive E POS;

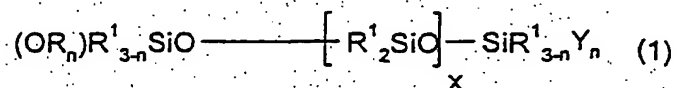
and in that the following are incorporated:

- o a catalytic system comprising a  
5 polyaddition metal catalyst (preferably of  
platinum nature) and optionally an  
inhibitor;
- o optionally one or more semireinforcing,  
nonreinforcing or bulking fillers;
- 10 o optionally water;
- o optionally one or more additives chosen  
from pigments, plasticizers, other rheology  
modifiers, stabilizers and/or adhesion  
promoters.

15 14. Method according to any one of Claims 1  
to 12, characterized:

in that a polycondensation  $SM_2$  is used which contains:

- at least one reactive silicone oil C POS  
whose crosslinking functional groups Fc  
20 react by polycondensation, these C POSs  
corresponding to the following formula (1):



in which:

- \*  $R^1$  represents monovalent hydrocarbon  
25 radicals which are identical or  
different, and Y represents

hydrolysable or condensable groups  $OR^{11}$   
 with  $R^{11}$  corresponding to the same  
 definition as that given above for  $R^c$ ,

- \*  $n$  is chosen from 1, 2 and 3 with  $n = 1$ ,  
 when  $R = H$  is a hydroxyl, and  $x$  has a  
 sufficient value to confer on the oils  
 of formula (1) a dynamic viscosity at  
 25°C of between 1 000 and  
 200 000 mPa.s,

this C POS being intended to react with  
 another C POS or with at least one  
 crosslinking agent  $D$ ,

- and/or at least one nonreactive E POS  
 different from the C POS(s);

and in that the following are incorporated:

- o a catalytic system comprising a  
 condensation metal catalyst;
- o optionally one or more semireinforcing,  
 nonreinforcing or bulking fillers;
- o optionally water;
- o optionally one or more additives chosen  
 from pigments, plasticizers, other rheology  
 modifiers, stabilizers and/or adhesion  
 promoters.

15. Method according to any one of Claims 1  
 to 12, characterized in that a polydehydrogeno-  
 condensation  $SM_3$  is used which contains:

- 5                   ▪ at least one  $C'$  type POS carrying hydroxyl crosslinking functional groups  $Fc'$  and/or  $OR'$  functional groups ( $R' = C_1-C_{30}$  alkyl,  $C_2-C_{30}$  alkenyl, aryl, optionally substituted (preferably halogenated)) precursor of the functional groups  $Fc'$ , these crosslinking functional groups  $Fc'$  being capable of reacting with other crosslinking functional groups  $Fb'$  ( $SiH$ ) of at least one  $B'$  type POS, this  $C'$  POS being taken alone or as a mixture with at least one nonreactive ( $E$ ) POS,
  - 10                   ▪ at least one reactive silicone oil  $B'$  POS, whose crosslinking functional groups  $Fb'$  are hydrogen functional groups, this  $B'$  POS comprising at least two  $\equiv Si-H$  groups per molecule (preferably at least three when the  $A$  POS comprises only two  $\equiv Si-Vi$  groups per molecule), these  $\equiv Si-H$  groups being

15                   advantageously present in the chain,
  - 20                   ▪ and/or at least one nonreactive  $E$  POS;
- and in that the following are incorporated:
- 25                   o a catalytic system comprising a polydehydrogenocondensation metal catalyst (preferably of platinum nature) and optionally an inhibitor;
  - o optionally one or more semireinforcing,

nonreinforcing or bulking fillers

- o optionally water;
- o optionally one or more additives chosen from pigments, plasticizers, other rheology modifiers, stabilizers and/or adhesion promoters.